

Production of Ammonium Sulfate Fertilizer from FGD Waste Liquors

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PROGRESS SUMMARY

In June of this quarter, two 50 gallon drums of ferrous EDTA scrubbing liquor were supplied by Dravo Lime Company (Fort Miami, OH plant) for continuing investigation of the precipitation of N-S containing crystals in the DDO configuration. In order to further study the influence of design variables on the size of Nitrogen-Sulfur (N-S) containing product crystals, another DDO run was carried out at a higher DDO ratio.

Using a DDO ratio of 20 in the current experimental run, the mass mean size of the crystals was found to be 250 μm , which is much higher than that found previously with a lower DDO ratio. The new liquor supplied by Dravo Lime Company was found to have a much lower pH (~ 4.5) compared to the previous supply (~ 6.8). The liquor was also found to contain higher amounts of sodium and sulfur. However, the liquor still produced N-S containing crystals, thus illustrating the robustness of the process.

Hydrolysis experiments were conducted in a one liter jacketed glass vessel, equipped with a temperature controller, using 1 M H_2SO_4 at 70° C and 80° C under atmospheric pressure. The purpose of these hydrolysis experiments was to evaluate kinetic information and to generate enough hydrolyzed liquor to produce NH_3 gas. The NH_3 gas is then used to neutralize the diluted sulfuric acid solution and precipitate pure ammonium sulfate crystals.

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1. INTRODUCTION

The process of making fertilizer grade ammonium sulfate requires the successful precipitation of N-S compounds from combining ferrous EDTA scrubbing liquor with a lime slurry. Following precipitation, the N-S containing double salt is hydrolyzed to generate the NH_4^+ ion. The hydrolyzed liquor could subsequently be neutralized with an ammonia solution to a desired pH before crystallizing $(\text{NH}_4)_2\text{SO}_4$. However, considering the current production cost, another process is being investigated. Instead of neutralizing the hydrolyzed liquor with a separate ammonia solution, it is possible to generate the ammonia gas by reliming the hydrolyzed liquor itself, and using this ammonia gas to neutralize the remaining hydrolyzed acid solution for the subsequent production of ammonium sulfate crystals. This process would lower the yield of ammonium sulfate, but could greatly lower the production cost.

2. CONTINUOUS PRECIPITATION OF NITROGEN-SULFUR CONTAINING COMPOUNDS (N-SCC) IN THE DOUBLE DRAW-OFF (DDO) CRYSTALLIZER

The description of the DDO crystallizer and its advantages are described in the previous report (Randolph, Mukhopadhyay, Unrau, Oct.-Dec. 1994). The purpose of the present study is to produce N-SCC from the ferrous EDTA scrubbing liquor for production of $(\text{NH}_4)_2\text{SO}_4$, and to examine the improvement in the crystal size distribution at a higher DDO ratio.

2.1. Experimental Procedure

The experimental set-up of a 7 liter DDO crystallizer is given in the previous report (Figure 7, Randolph, Mukhopadhyay, Unrau, Oct.-Dec. 1994). The feed scrubbing liquor and lime slurry flow rate were chosen as to retain a residence time of approximately 60 minutes, to be

consistent with the previous runs. The present source of scrubbing liquor was found to be more acidic (pH ~ 4.5) compared to the previous supply (pH ~ 6.8). Therefore, the lime flow rate was increased at the expense of the feed flow rate (to keep the vessel residence time at 60 minutes). The overflow of the crystallizer was continuously drawn off via an inverted 3.5 x 30 cm glass cone tube. The underflow from the crystallizer was set to discharge at long time intervals with a higher flow rate to avoid clogging the discharge line. The mixture of underflow and overflow represent the true product from the vessel. The product from the DDO crystallizer was filtered, and dried for evaluation of the slurry density. The crystals were sieved for size analysis by a sonic sifter. The crystal samples were also examined for their morphology and chemical composition.

2.2. Results and Discussion

The mean vessel residence time (τ) for the DDO run was 54.0 minutes. The initial pH of the reactor slurry was ~4.5. During the experiment the pH was controlled around a set point of 8.3. The underflow (Q_u) and overflow (Q_o) were controlled to obtain a DDO ratio ($R = (Q_o + Q_u)/Q_u$) of approximately 20. Observations revealed the DDO ratio has a profound influence on both the slurry density and on the crystal mass mean size. Table 1 displays the slurry density of crystalline product at various DDO ratios. It is interesting to note that the slurry density increased by 10 g/L as the DDO ratio increased from 10 to 20. The cumulative weight of the N-SCC crystals at various size ranges (as obtained from size analysis) is shown in Figure 1. The mass mean size of the N-S containing crystals is found to be 250 μm (Figure 1). This is a very encouraging result which signifies the importance of the DDO crystallizer configuration versus the use of the MSMR configuration. However, at the higher DDO ratio of 20, a poor mixing pattern was observed, most likely due to the increased slurry density.

The population density of the N-SCC crystalline precipitates at various size ranges is given in Figure 2. The photomicrographs of the precipitated N-SCC crystals are shown in Figures 3-5. Figure 3 shows the morphology of N-S containing crystals in the product slurry. A picture of the crystals on sieve number 13 (size ~ 250 μm) is shown in Figures 4 and 5 at magnifications of 40X and 100X, respectively. In these pictures, the crystals seem to be in an agglomerated form.

3. HYDROLYSIS OF NITROGEN-SULFUR CONTAINING COMPOUNDS

The hydrolysis chemistry of N-SCC has been discussed in a previous report (Randolph, Mukhopadhyay, Unrau, Oct.-Dec. 1994). The aim of the present hydrolysis experiments is to evaluate the kinetics and to generate sufficient liquor for the crystallization of $(\text{NH}_4)_2\text{SO}_4$.

3.1. Experimental Procedure

The experimental set up for hydrolysis experimentation has been described in a previous report (Randolph, Mukhopadhyay, Unrau, Oct.-Dec. 1994). About 10 grams of uniformly sized dry N-SCC crystals were added to 500 ml of 1 M H_2SO_4 , which had been preheated to the desired temperature. The hydrolysis experiment was carried out at 70° C and 80° C. Samples were withdrawn and sent to Copper State Analytical Laboratory in Tucson for analysis of ammonia-nitrogen. The ammonia-nitrogen concentration was calculated according to EPA method number 4500-NH3F.

3.2. Results and Discussion

The concentration of NH_4^+ ion in the solution is calculated from the total ammonia-

nitrogen concentration. The progress of the hydrolysis reaction versus time has been plotted in Figures 6 and 7 for each experiment. A comparison of the degree of hydrolysis of N-SCC at 70°, 80° and 95° C are given in Figure 8. The hydrolysis data (Figures 6-8) indicate the rate of hydrolysis is faster at higher temperatures. Hence at 16 hours and 95° C, hydrolysis was accomplished completely, whereas only 35% hydrolysis could be achieved during the same time at 70 °C.

4. OPTIMIZATION OF DDO PARAMETERS BY COMPUTER SIMULATION

Further computer simulations were run to optimize crystal growth and nucleation rate DDO parameters. All data in this section were obtained solely through theoretical computer simulation. In the following discussion an understanding of MSMPR and DDO crystallizer operation by the reader is assumed. As before (Randolph, Mukhopadhyay, Unrau, Jan. - Mar. 1995), the crystal growth and nucleation rate equations used were:

$$G = k_G s^a$$

$$B^\circ = k_N G^i M_T^j,$$

respectively. Where,

G = growth rate

k_G = growth rate constant

s = supersaturation

a = exponent linking growth rate to supersaturation

B° = nucleation rate

k_N = nucleation rate constant

i = exponent linking nucleation rate to growth rate

M_T = suspension density

j = exponent linking nucleation rate to suspension density, (White and Randolph, 1989).

The same computer program was used to simulate these studies (Randolph and Sutradhar, 1992). For these simulation studies, values of $i = 2.0$ and $j = 0.5$ from the previous runs were used. The adjusted parameters include the DDO ratio (R), the residence time in minutes (τ), and the crystal fines cut-off size (L_f). Crystal fines cut-off sizes of 30, 45, 60, and 100 μm were used with ranges of 6 to 22 for R , and 30 to 180 minutes for τ . Recall the equation used to calculate the dimensionless cut-off size, X_f , which was used as an input to the program:

$$X_f = L_f / (G_o \tau).$$

Where,

L_f = crystal fines cut-off size

G_o = MSMPR crystal growth rate

τ = reactor residence time, (Randolph and Sutradhar, 1992).

Note that X_f is affected by both L_f and τ ; this is accounted for in the plotted data. Again, output was obtained for the mass mean size ratio, crystal growth rates, slurry densities, and DDO per pass yield. Plots were obtained for mass mean size versus DDO ratio for varying residence times and crystal fines cut-off sizes. In the simulations, the mass mean size ratio, $L_{4,3}/L_{4,3o}$, is a ratio of the DDO mass mean size to that of the MSMPR (denoted by the subscript "o") mass mean size. For the following discussion please refer to Figures 9 through 12.

In all four figures, the mass mean size ratio increased as the DDO ratio increased, and as the residence time decreased. Larger mass mean size ratios resulted when bigger crystal fines cut-off sizes were used. Hence, the largest mass mean size ratio, 8.04, occurred with a DDO ratio of 22, a residence time of 30 minutes, and a cut-off size of 100 μm . An explanation of these trends is as follows. The large cut-off size (100 μm) means the remaining crystals in the DDO crystallizer will be of a bigger mass, thus increasing the mass mean ratio. An increase in the DDO ratio will increase the mass mean size by lengthening the crystal growth time allowed for the larger crystals, and removing more of the crystal fines.

For the smaller residence times (30 to 60 minutes) there is a large mass mean size ratio, and for the larger residence times (greater than 60 minutes) the mass mean size ratio decreases. This is because for small residence times, the DDO configuration results in a large improvement in crystal mass mean size versus the MSMPR configuration (up to 8 times larger for higher cut-off sizes). The growth rate is inversely proportional to the residence time, and since the DDO configuration removes the smaller crystals, the growth continues on the already formed nuclei, resulting in a larger crystal mass mean size for the DDO crystallizer.

For larger residence times, the DDO configuration still results in a larger crystal mass mean ratio versus the MSMPR configuration (up to 4 times larger for higher cut-off sizes), but the large residence time allows more growth to occur in the MSMPR crystallizer, hence the ratio is lower than for small residence times. A note of clarification, the larger mass mean ratio for small residence times does not imply larger crystals exist for the smaller residence times, just that there is a larger difference in crystal mass mean size between the DDO and MSMPR configurations at smaller residence times.

Currently, the DDO set up runs at approximately a 30 to 45 μm crystal fines cut-off size. With a residence time of one hour, it is seen that a larger DDO ratio will yield a higher mass mean size versus the MSMPR configuration (see Figures 9-12).

In conclusion, these simulations show increasing the DDO ratio and/or decreasing the residence time result in increasing the mass mean size ratio (DDO to MSMPR). A larger crystal fines cut-off size will result in a larger crystal mass mean size ratio. The crystal fines cut-off size trend (increasing the crystal fines cut-off size increases the crystal mass mean ratio) agrees with the previously found trend (Randolph, Mukhopadhyay, Unrau, Jan. - Mar. 1995). Furthermore, some experimental data were used to confirm the computer simulated trends relating an increasing DDO ratio to an increase in the crystal mass mean size ratio.

The results described in section 4 are strictly from theoretical simulations. All values used in the simulations were chosen as ranges, not from any experimental data.

References

Randolph, A. D., Mukhopadhyay, S. and Unrau, E. "Production of Ammonium Sulfate Fertilizer from FGD Waste Liquors", DOE Quarterly Technical Report, October-December 1994.

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White, E. T. and Randolph, A. D. "Optimum Fines Size for Classification in Double Draw-Off" Crystallizers, *Ind. Eng. Chem. Res.*, 28, 276-284, 1989.

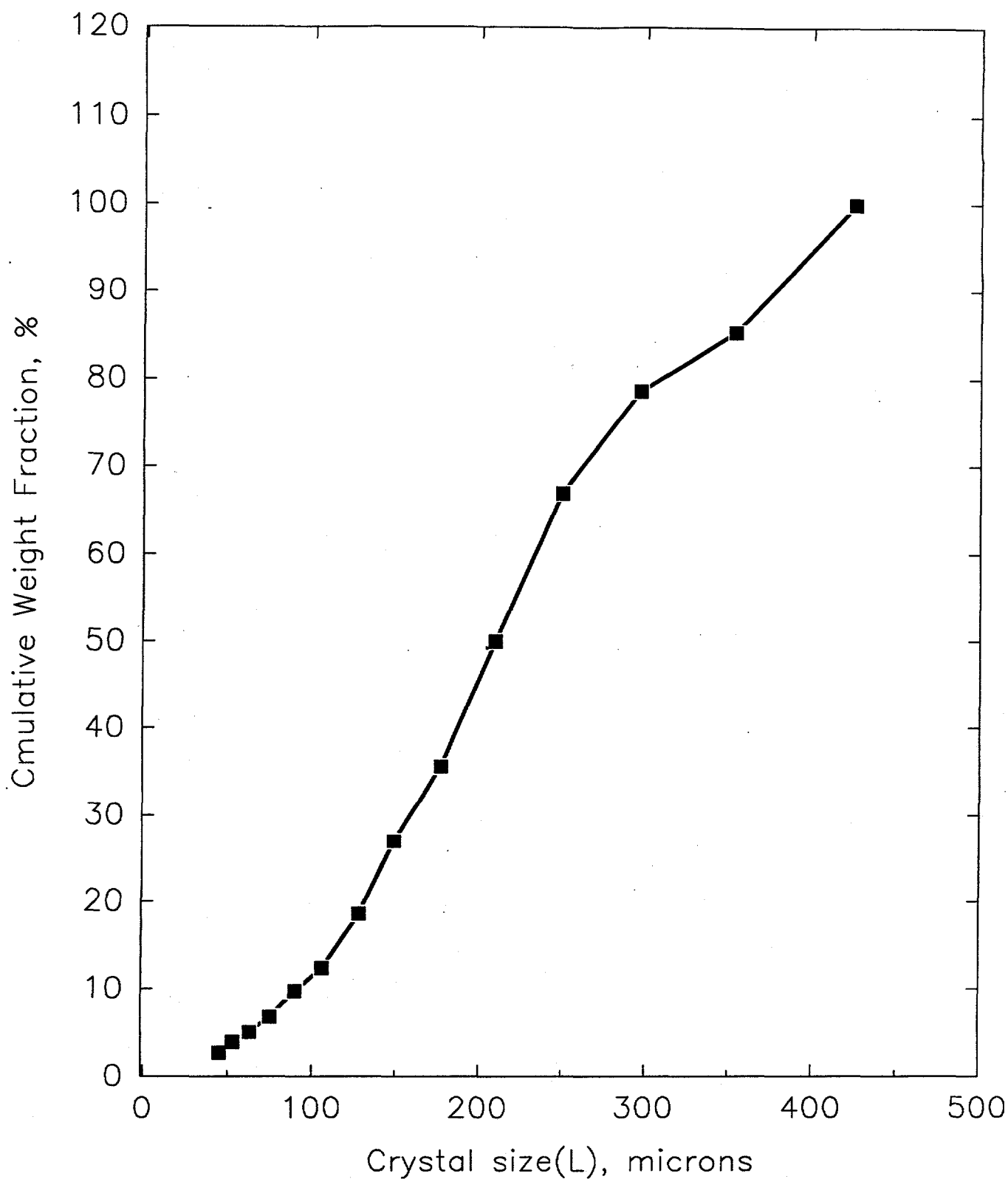


Figure 1. Cumulative weight fraction vs. size of the N-S containing crystals obtained from DDO crystallizer

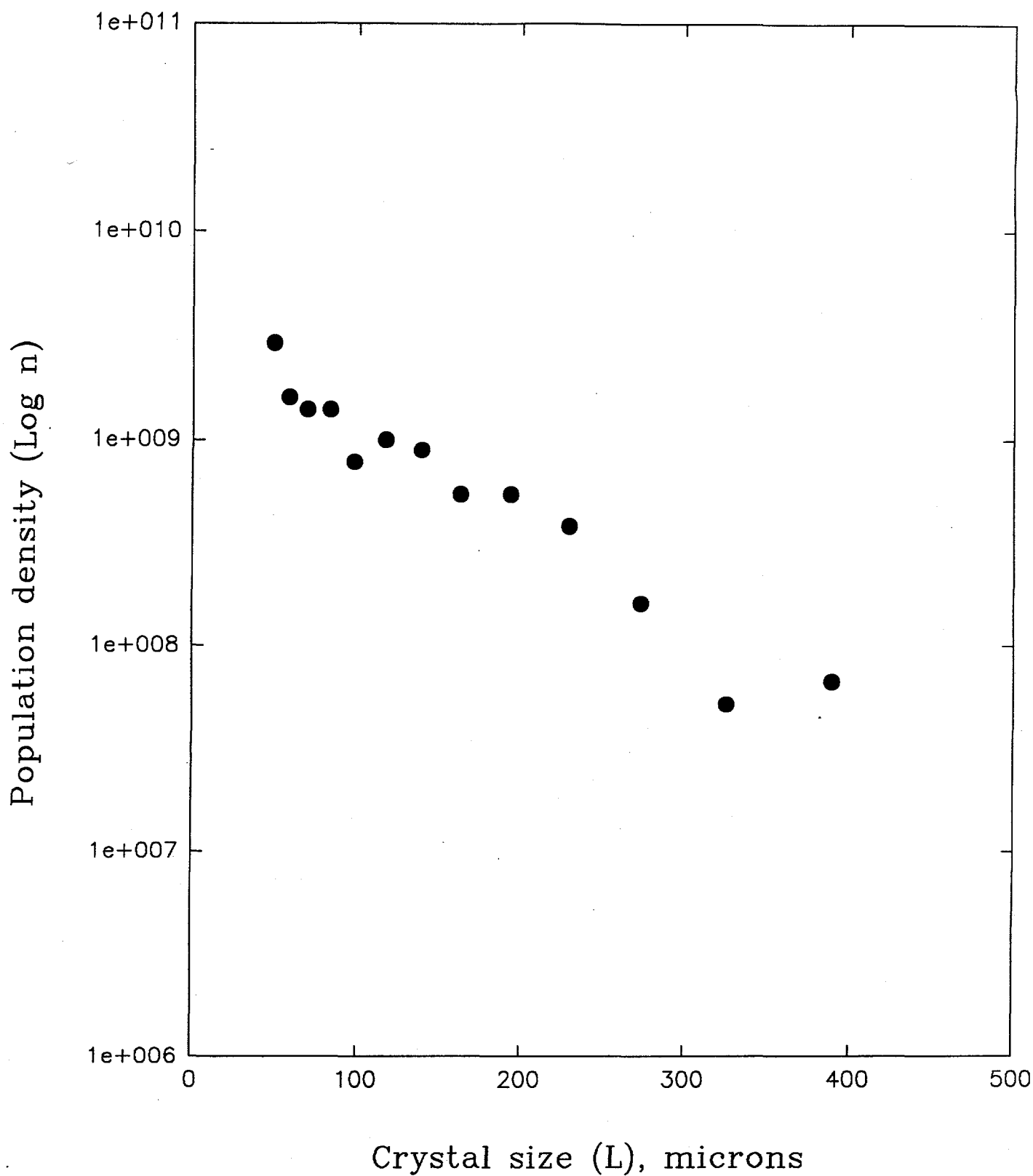


Figure 2. Population density vs. size of N-S crystals obtained from DDO crystallizer by reaction of FGD waste liquor with Dravo lime



Figure 3. Morphology of N-S containing double salt of Ca and Na obtained from DDO run
(Magnification = 40X)

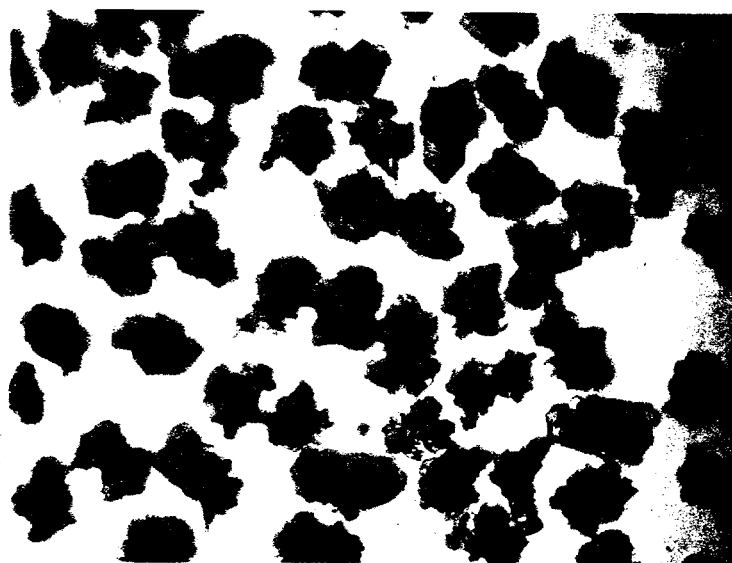


Figure 4. Photomicrograph of N-S containing crystals retained on sieve #13 during size analysis
(Magnification = 40X)



Figure 5. Photomicrograph of N-S containing crystals retained on sieve #13 during size analysis
(Magnification = 100X)

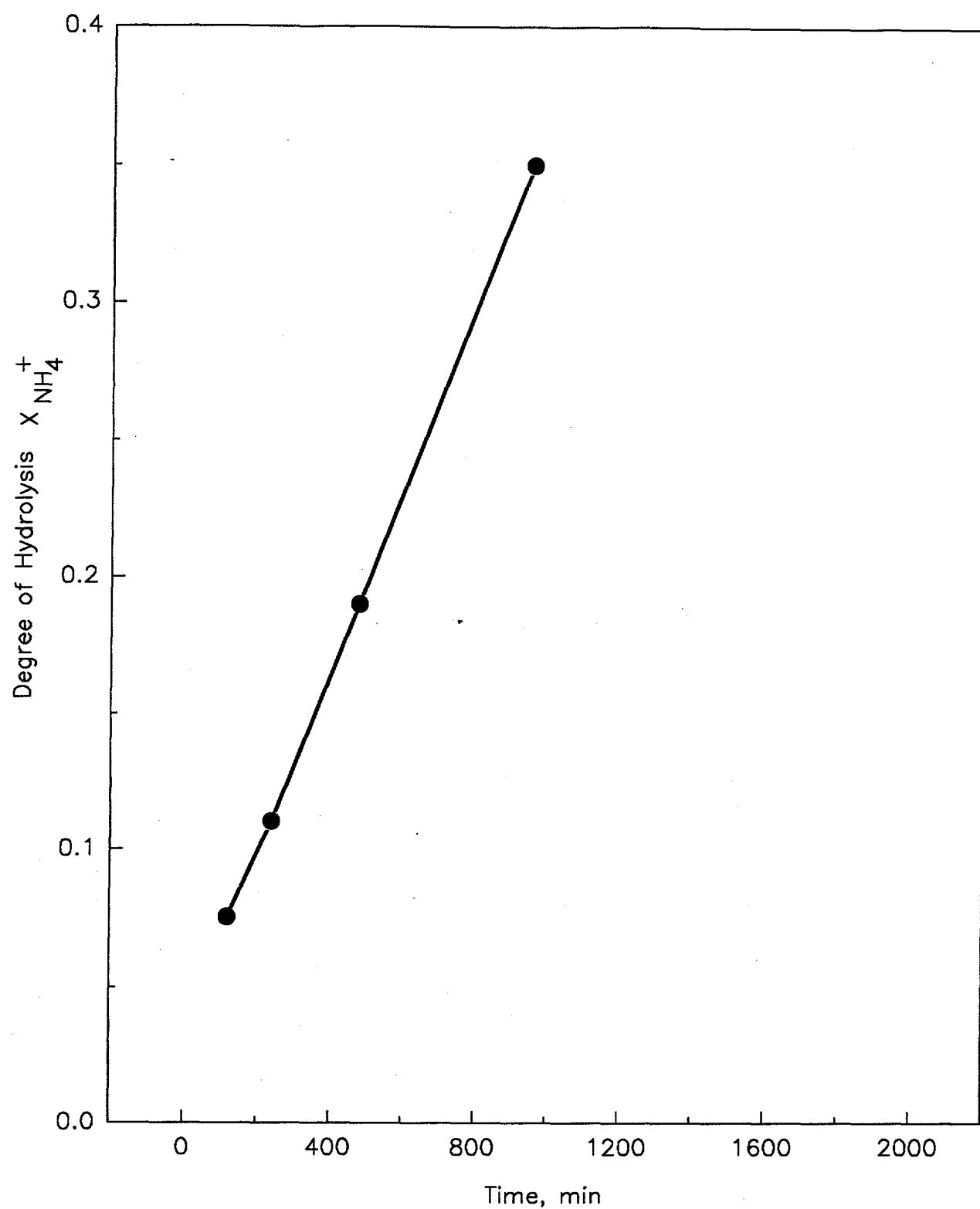


Figure 6. Progress of hydrolysis of N-S Compound with time in 1M Sulfuric Acid Solution at about 70°C

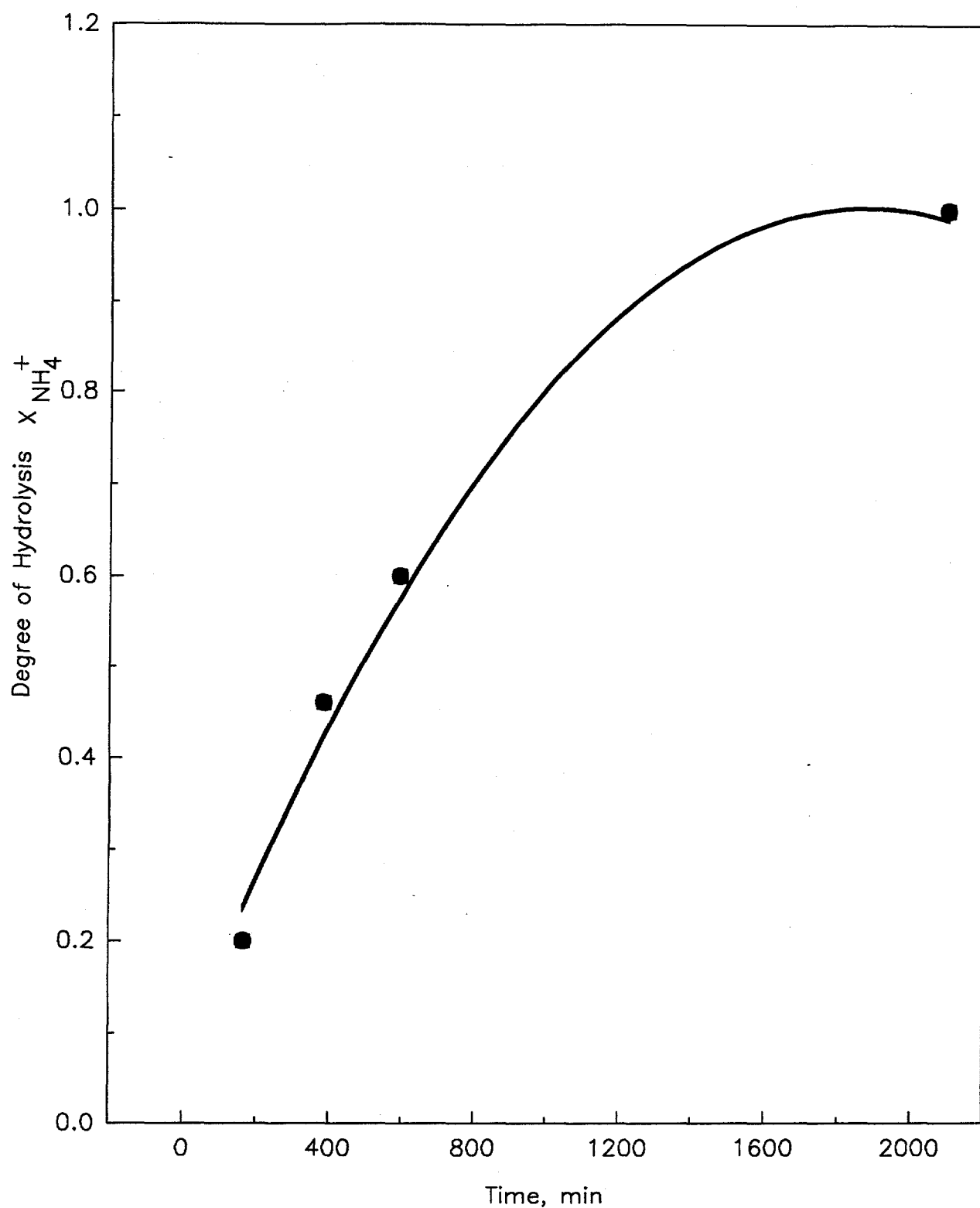


Figure 7. Progress of hydrolysis of N-S Compound with time in 1M Sulfuric Acid Solution at about 80°C

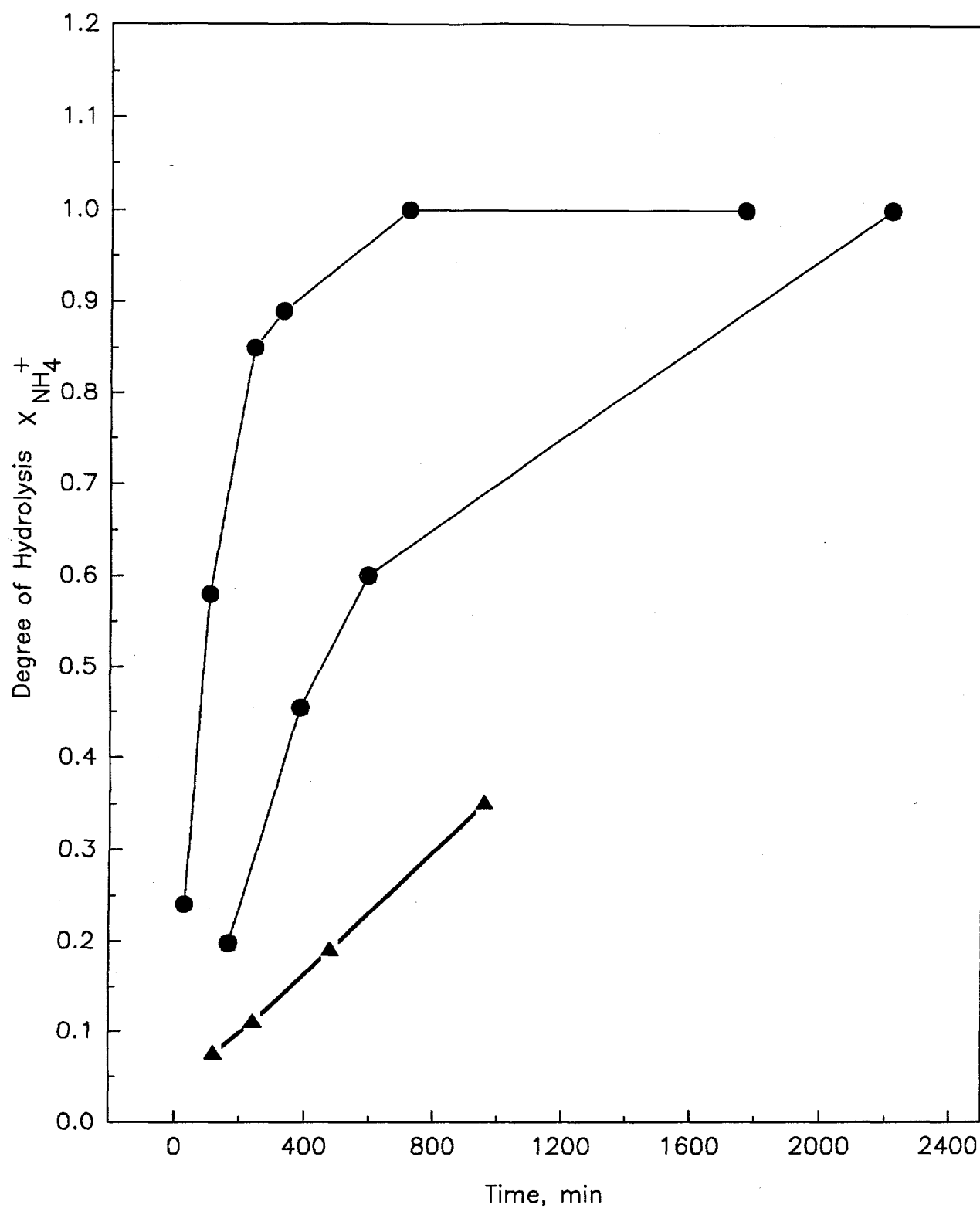


Figure 8. Comparison of hydrolysis of N-S Compound in 1M Sulfuric Acid Solution at 70, 80 and 90°C

Mass Mean Ratio vs. DDO Ratio

Cut-Off Size = 30 microns

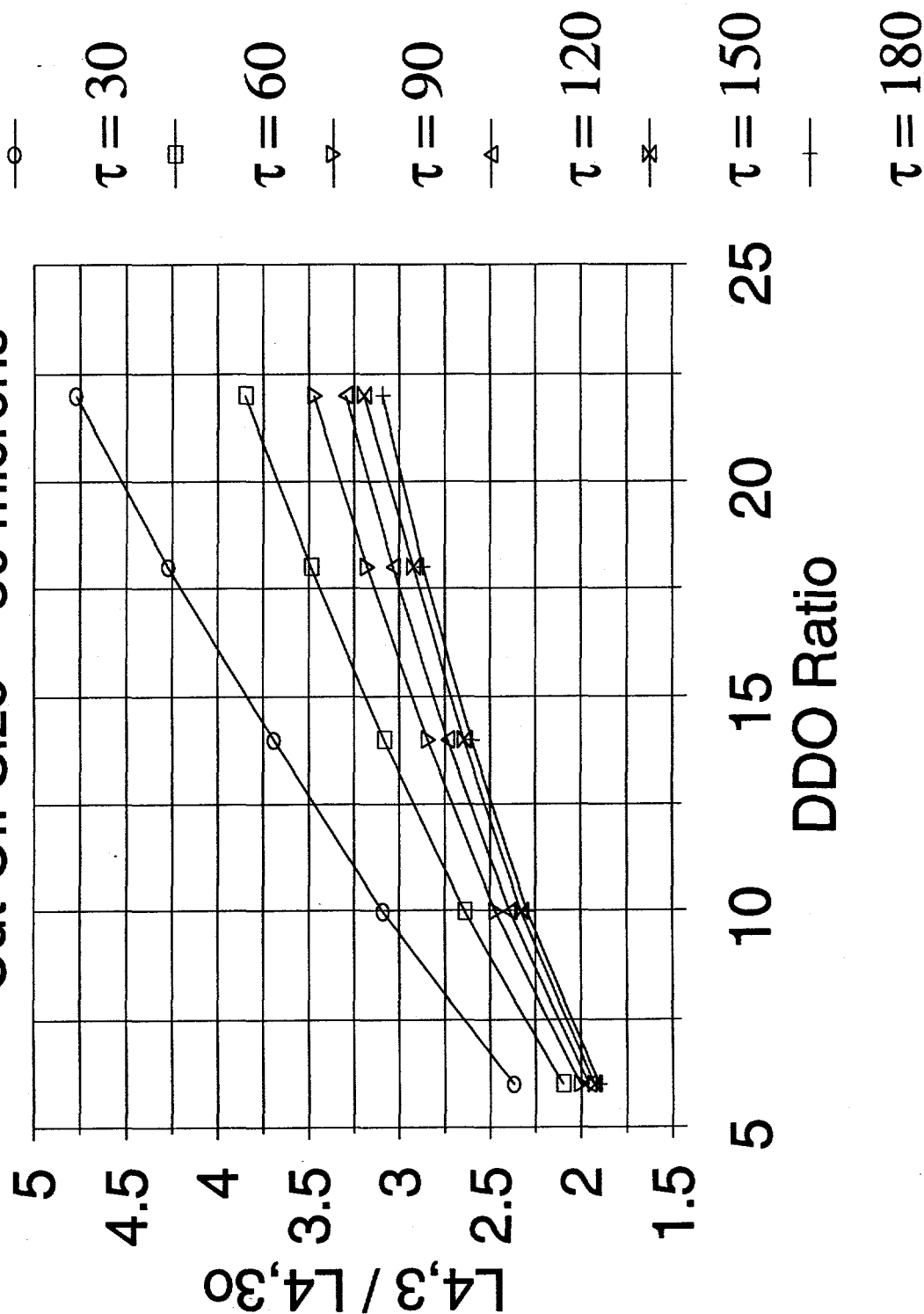


Figure 9.

Mass Mean Ratio vs. DDO Ratio

Cut-Off Size = 45 microns

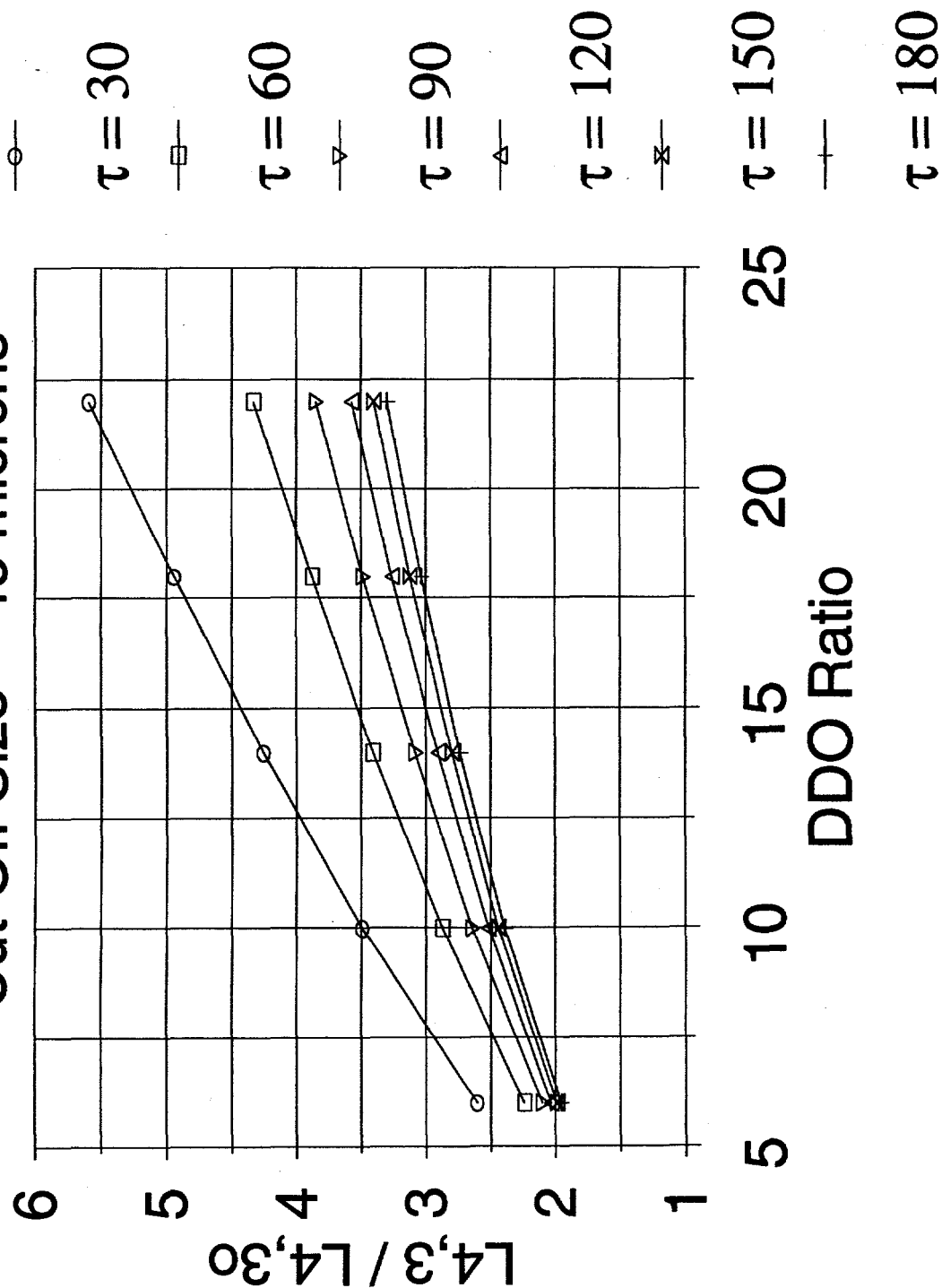


Figure 10.

Mass Mean Ratio vs. DDO Ratio

Cut-Off Size = 60 microns

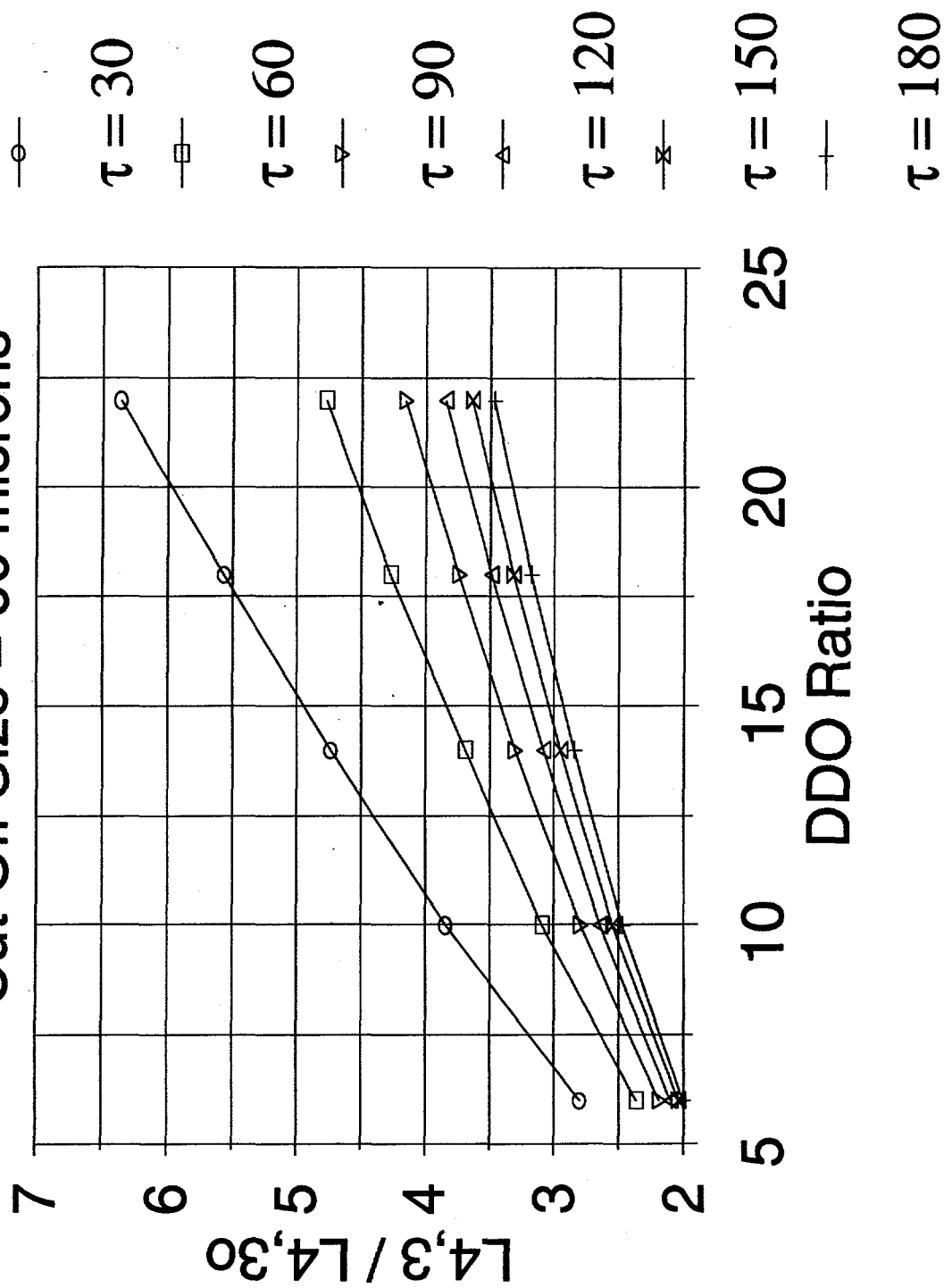


Figure 11.

Mass Mean Ratio vs. DDO Ratio

Cut-Off Size = 100 microns

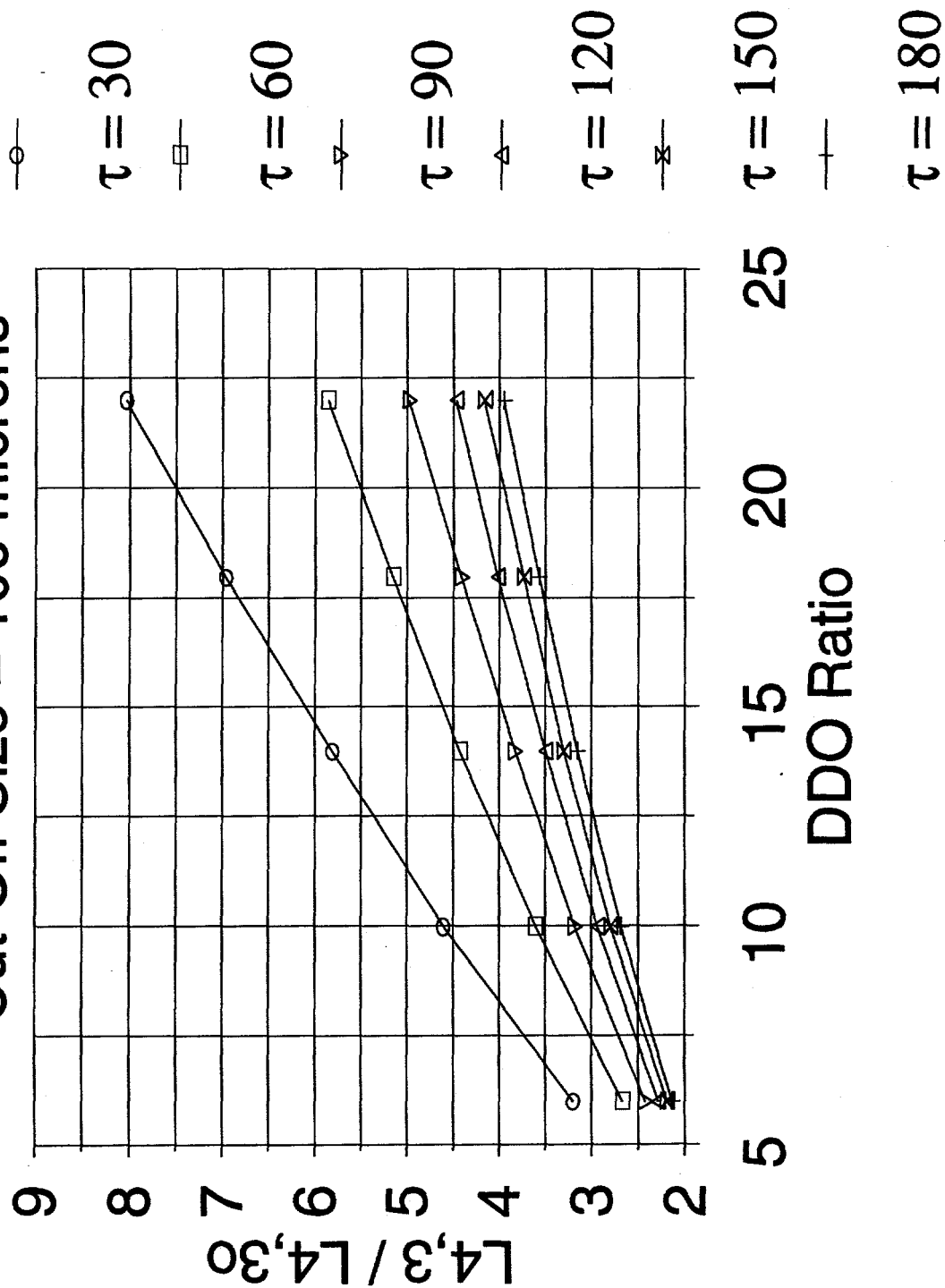


Figure 12.

Table 1. Slurry Density of N-S Containing Crystals at Various DDO Ratio

DDO Ratio	Slurry Density, g/L
10	40.58
15	45.09
20	49.02